**BIO ETHERS**

**THE ADVENT OF COBLENDING**

**HARVESTING THE ETBE ETOH SYNERGY**

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Chairman Biofuels of European Fuel Oxygenates Association

*2nd Green Refining & Petrochemicals Forum*

Dubrovnik - Croatia – 17 June 2011
BioFuels: 3 Key Entities

- Italian Biofuels Technology Platform
- Italian Chemical Industry Federation
- European Fuel Oxygenates Association
Italian Bio-fuels Platform: Organizational Structure

- General Assembly
- Steering Committee
  - Technical Secretariat
- Scientific Committee
  - Biomass WG1
  - Conversion WG2
  - Use WG3
  - Sustainability WG4
  - Economy WG5

http://www.unibo.it/Portale/Ricerca/Servizi+Docenti+Ricercatori/finanzeuropei/biofuelsitalia.htm
Federchimica and Italian Chemical Industry

Federchimica is the National Federation of Chemical Industry.

Chemical Industry Italy:
- Enterprises 2900
- Production Units 3500
- Turn-over (2009) (G€) 46
- Employees 119,000

Federchimica:
- Member Companies 1,300
- Employees 90,000
- Sector Groups 41
- Associations 16
- Enterprises w/i GFR 18

Federchimica is member of Confindustria and CEFIC

www.federchimica.it
## Renewable Sources Group\(^*\) of Federchimica: Represented Activities

18 Enterprises as per March 2011

<table>
<thead>
<tr>
<th>Energy Uses</th>
<th>Non-Energy Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bio-Fuels, and Bio-Components for Fuels, Production</td>
<td>Transformation of Renewable Raw Materials</td>
</tr>
<tr>
<td>- [bio-alcohols (ethanol, butanol)]</td>
<td>- Additives, Chemical Intermediates</td>
</tr>
<tr>
<td>- [bio-ethers (ETBE, TAAEE)]</td>
<td>- Starch and Derivatives</td>
</tr>
<tr>
<td>- [bio-esters (FAME, FAEE)]</td>
<td>- Biorefineries</td>
</tr>
<tr>
<td>- [BTL (Biomass To Liquid)]</td>
<td>- Oleochemicals</td>
</tr>
<tr>
<td>(complementary) Production of Energy from Renewable Sources</td>
<td>- Polymers</td>
</tr>
<tr>
<td>- Vegetable Oils</td>
<td>- Bio-cosmetics</td>
</tr>
<tr>
<td>- Bio-gas</td>
<td>- Solar</td>
</tr>
</tbody>
</table>

http://www.federchimica.it/Federchimica/AssociazioniSettore/AISPEC.aspx
European Fuel Oxygenates Association

- Non-profit Technical Organisation
- Founded in 1985
- ~ 2/3rd of Total EU Etherification Capacity

http://www.efoa.eu
Bio-Ether (ETBE) is for Petrol, what Bio-Ester (FAME) is for Gasoil.

ORIGIN

Bio-Mass

PRIMARY

Bio-Ethanol
Bio-Oil

DERIVED

Bio-Ethers
Bio-Esters
Bio-HCs

FUEL

Petrol
Gasoil
European Fuel-Ethers Production Capacities 2011 (KT/Y)

- ALGECIRAS 54
- BILBAO 74
- HUELVA 50
- LA CORUNA 52
- TARRAGONA a 54
- TARRAGONA b 71
- SINES 50
- ANTWERP a 183
- ANTWERP b 270
- FEYZIN 56
- FEYZIN 84
- DUNKERQUE 65
- FOS SUR MER 612
- GONFREVILLE 75
- ASPROPYRGOS 65
- ASPROPYRGOS 128
- CORINTH 45
- PORTO 115
- PORTO 110
- FAWLEY 122
- GRIMSBY 100
- KILLINGHOLME 82
- MARL 250
- SCHWEDT 385
- SCHWEDT 160
- VOHBURG 37
- WESSELING 65
- BOTLEK 591
- EUROPORT 98
- GELEEN 138
- PERNIS 153
- COLOGNE 31
- HEIDE 12
- KARLSRUHE 163
- SCHWEDT 160
- VoHburg 37
- WESSELING 65

Planned: MTBE, ETBE, TAME, TAEE, Planned.
Co-blending ETBE & ETOH
Key Tool for EU Member States to Address Bio-energy Challenge: The Example of Germany
Legal “Bio-Drivers”

  - ≥ 10% bio-energy in fuels

  - ≥ 6% CO\textsubscript{2} emissions reduction in fuels WTW

- DE National Bio-energy Obligation
  - ≥ 2.80% in Petrol (2009 – 2014)
  - ≥ 4.40% in Gasoil (2007 – 2014)
  - ≥ 6.25% in Petrol + Gasoil (2010 – 2014)

- DE Non-compliance Penalty (2011)
  - 43 €/GJ\textsuperscript[*] for Petrol
  - 19 €/GJ\textsuperscript[*] for both Gasoil and cumulative (P+G)

\textsuperscript[*] bio-energy blending shortfall
### Addressing RED & FQD

**EU Directives Challenge**

### What
- 10% Bio-energy in Fuels (RED)
- 6% CO₂ Saving (FQD)

### How
- CO₂ Reduction Effectiveness of Bio-components
- High Bio-components Blending Percentage
- Exploitation "best seller" Petrol Grade (Protection Grade)

### Challenge
- Consumers Acceptance of High-Bio Grades (E10)
- Existing Vehicle/Engines Compatibility/Operability
- Fuel Specifications Limits (Oxygenates/Oxygen/FAME)
- Financial Implications (Costs/Economics)

### Solution
- Adopting Consolidated Solutions (Fuel-Ethers)
- Maximizing Actual Bio-energy Blending within E5
- Optimizing Logistics & Minimizing Investments (ETBE-BOB)
- Capturing Bio-components' Well-to-Wheels CO₂ Saving Potential
- Harvesting Bio-components' Synergetic "Non-linear" Effects
ETBE: A Multifaceted Benefits Carrier
..and “Co-blending” further offers Additional Specific Benefits!

- Blending more Bio-energy within Petrol Specs Limits
- Capturing Bio-components' Well-to-Wheels CO₂ Saving Potential
- Minimizing Quality “Give-away” and fossil base-stock cost, via ETBE-containing “Dual BOB” for E5/E10
- Harvesting Synergetic "Non-linear" Effects of Bio-components
German Bio-energy Targets and E5 Blend “Options”

- 5%v/v ETOL
- 15%v/v ETBE
- E5 Co-blend
- B7

- Fuel-type-specific target
- Maximum bio-energy contribution above minimum target
- Excess from B7 available for petrol (excluding B100 contribution)
- Residual Gap to cumulative target (excluding B100 and E85 contribution)
53% more bio-energy into E5 via “Co-blending”

- 5.11
- 3.34

Residual contribution from biodiesel exceeding bio-energy cumulative target in gasoil (B7)
Maximum bio-energy contribution
Residual Gap to cumulative target (excluding B100 and E85 contribution)
53% more bio-energy into E5 via “Co-blending”

<table>
<thead>
<tr>
<th></th>
<th>“Alcohol-only” Ethanol</th>
<th>“Ether-only” ETBE</th>
<th>“co-blending” ETBE+ETOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limiting Petrol Spec.</td>
<td>5% v/v ETOH</td>
<td>15% v/v ETBE</td>
<td>2.7% m/m O₂</td>
</tr>
<tr>
<td>Bio-energy Content</td>
<td>3.3%</td>
<td>4.6%</td>
<td>5.1%</td>
</tr>
<tr>
<td>ETBE Content</td>
<td>0%</td>
<td>15%</td>
<td>5.55%</td>
</tr>
<tr>
<td>Oxygen Content</td>
<td>1.8%</td>
<td>2.3%</td>
<td>2.7%</td>
</tr>
<tr>
<td>O₂ Limit Exploitation</td>
<td>68.2%</td>
<td>86.3%</td>
<td>100%</td>
</tr>
</tbody>
</table>
E5: “Co-blending” Enables Significant Non-compliance Penalty Saving

“Alcohol-only” Ethanol

“co-blending” ETBE+ETOH

Bio-energy Content

%e/e

3.3

5.1

Additional Penalty Avoidance Value

€/\text{TPET}

0

14.0

Mill-€/\text{Y}

0

21.0

€/\text{ETBE}

0

254

[1] On top of what achievable with 5%v/v ETOH directly blended into E5 “Protection Grade”
[2] Example based on an average refinery petrol production of 1.5 million tons per year
ETBE: Two Relevant CO₂ Saving Contributions

65% \hspace{1cm} +54% \hspace{1cm} 35%^{[1]} \hspace{1cm} 100% \hspace{1cm} 0.618 \hspace{1cm} 0.335 \hspace{1cm} = 0.953

\[ T_{CO2}/T_{ETBE} \]

[1] Key ETBE blending properties, like vapour pressure, distillation characteristics and octane contribution, affecting fuel formulation, reduce refinery operations’ CO₂ emissions, by reducing carbon and aromatics content as well as the use of refinery fuel.

[2] Based on CO₂ cost at current ETS value of 20 €/T_{CO2}
ETBE Further Reduces CO₂ Emissions

HART July 2007

“Best results by far are obtained when ethanol is converted to bio-ETBE. The use of ETBE can allow the saving of 4 times the primary energy required to produce its fossil alternative. IFEU recommends to exploit the whole potential of bio-ETBE.”

CE-Delft October 2007

“ETBE and Ethanol: A Comparison of CO₂ Savings

Report
Delft, October 2007

Author(s): Harry Croesen, Bettina Kampmen, Gerdjan van de Vroede, Maartje Severink

“This study indicated that, when bio-ETBE is used, the resulting modification of refinery operations determine a significant reduction of greenhouse gases emissions.”

IFEU August 2008

“Best results by far are obtained when ethanol is converted to bio-ETBE. The use of ETBE can allow the saving of 4 times the primary energy required to produce its fossil alternative. IFEU recommends to exploit the whole potential of bio-ETBE.”

“ETBE Further Reduces CO₂ Emissions”

“ETBE Further Reduces CO₂ Emissions”

“ETBE Further Reduces CO₂ Emissions”

“The use of bio-ETBE reduces refining crude-oil need and processing intensity, requires less fuel and, implying relevant petrol composition changes, allows the reduction of carbon factor and lesser CO₂ emissions”
“Dual” BOBs for E5 and E10

BOBcb = ETBE-containing E5/E10-dual-BOB that, when blended with 5%v/v ETOH, yields E5 @ 2.7%m/m O₂
BOBdb = Oxy-free E5/E10-dual-BOB, yielding E5 with 5%v/v ETOH, and E10 with 10%v/v ETOH
E5cb = E5 petrol (protection grade) “co-blend” ETBE/ETOH – 2.7%m/m O₂
E10cb = E10 petrol “co-blend” ETBE/ETOH – 3.7%m/m O₂
E5db = E5 petrol containing only ETOH @ 5%v/v
E10bd = E10 petrol containing only ETOH @ 10%v/v
Conservatively neglecting positive non-linear “co-solvency” effects of ETBE
In order to be used for both E5 and E10 petrol grades, and due to the non-linear blending volatility behaviour of ethanol, the oxygen-free dual-BOB has to feature lower than specification volatility, to ensure RVP specs compliance of E5. This unwanted effect doesn’t occur with ETBE-containing dual BOB.
Co-blending Addresses ETOH E70 Boost

- **BOB**
  - Fossil HC Blendstock

- **E5db**
  - E5 Grade ETOH-only 5%v/v

- **E5cb**
  - E5 Grade Co-blend ETOH/ETBE

- **E10db**
  - E10 Grade ETOH-only 10%v/v

- **E10cb**
  - E10 Grade Co-blend ETOH/ETBE

E70 (%) Evaporated @ 70 °C

- **-6.4** (absolute)
- **-40%** (increase)
Conclusion

Harvesting the synergy of co-blending bio-ETBE and bio-Ethanol, represents an effective, immediate and practical avenue to address both EU and MSs ambitious bio-fuel targets. It actually enables higher bio-energy content, while both enhancing environmental benefits and improving operators flexibility.